ARMY RESEARCH LABORATORY

HPSEC Analysis of Ester-Based Polyurethane Rubber Materials

by Eugene Napadensky, Gary L. Hagnauer,
Amy Kinkennon, and Donald T. Rorabaugh

ARL-TR-2201   April 2000

20000530 031

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

HPSEC Analysis of Ester-Based Polyurethane Rubber Materials

Eugene Napadensky, Gary L. Hagnauer, and Amy Kinkennon
Weapons and Materials Research Directorate, ARL

Donald T. Rorabaugh
U.S. Army Armament Research, Development, and Engineering Center

Abstract

The work described in this report contributes to a larger study conducted by the U.S. Army Tank-automotive and Armaments Command (TACOM) at Picatinny Arsenal, NJ, to evaluate the environmental and operational stability of candidate commercial polyester-polyurethane rubber materials for possible fuel bladder and containment applications. High-performance size-exclusion chromatography (HPSEC) techniques are employed to analyze and help understand the effects of accelerated environmental exposure on the average molecular weights (MW) and molecular weight distributions (MWD) of the rubber in selected test specimens. A special test method and sample preparation procedures to extract and isolate the soluble polymer in test specimens from coating, interlayer, fabric, and carbon reinforcement components are described. HPSEC separates polymer molecules according to their relative "sizes" in solution and therefore is very useful in studying rubber reversion and estimating the extent of polymer degradation due to chain scission processes. Exposure to elevated temperature and moisture content (percent relative humidity) accelerate sample degradation. As the aging time and severity of aging conditions increase, gel formed during the early stages of exposure disappears and the MW of soluble materials continues to decrease. The chemical mechanism for polymer chain degradation and possible cause and consequences of the gelation effect are discussed.

Table of Contents

INTENTIONALLY LEFT BLANK.

List of Figures

List of Tables

v

INTENTIONALLY LEFT BLANK.

1. Introduction

1.1 Background and Objective. The U.S. Army Tank-automotive and Armaments Command (TACOM) at Picatinny Arsenal, NJ, is interested in the environmental and operational stability of polyester-polyurethane rubber materials for possible fuel bladder and containment applications. TACOM conducted an extensive environmental aging and testing program to evaluate candidate materials[1] and was interested in the application of high-performance size-exclusion chromatography (HPSEC) for analyzing the molecular weights of ester-based polyurethane rubber specimens before and after accelerated environmental aging. The objective of this study is to employ HPSEC to determine the effects of selected time, temperature, humidity, and fuel immersion conditions on molecular weight and thereby evaluate the reversion or degradation characteristics of the rubber in test specimens.

1.2 Specimen Identification. Code numbers representing specimen batch, exposure time, temperature, and relative humidity identify environmentally aged and unaged (Control) rubber specimens. There are three specimens provided per each set of exposure conditions, and the specimens are of standard size (approximately 1 in × 6 in) used for tensile and/or lap shear testing. The Control specimens are identified as

- Batch 1 room temperature (CT1R1 and CT1R2) and 180° F temperature (CT1H1 and CT1H2) test or HPSEC Control Specimen Batch 1 Designation = Control No. 1.

- Batch 2 room temperature (CT2R1 and CT2R2) and 180° F temperature (CT2H1 and CT2H2) test or HPSEC Control Specimen Batch 2 Designation = Control No. 2.

Environmentally aged specimens are described in the following paragraphs.

---

[1] Rorabaugh, D. T., D. A. Martinelli, and A. Mock. "Polyurethane Fuel Cell Bladder Stability Evaluation." Laboratory Report No. 411, U.S. Army Armament Research, Development, and Engineering Center, Picatinny Arsenal, NJ, November 1997.

Batch 1 samples subjected to 180° F/80% RH + 7-day immersion in JP5 fuel at room temperature and tested at room temperature are designated B1115FR(1,2,3), and B1120FR(1,2,3), indicating 115- and 120-day exposure, respectively. The numbers in parentheses indicate replicate test specimens and therefore are not expected to have any significant differences when analyzed by HPSEC. The HPSEC designations for specimens B1115FR(1,2,3) and B1120FR(1,2,3) are

- B115/180/80 = Batch 1, 115 days at 180° F/80% RH + 7 days in JP5 fuel at RT
- B120/180/80 = Batch 1, 120 days at 180° F/80% RH + 7 days in JP5 fuel at RT.

Batch 1 samples subjected to 180° F/95% RH and tested at 180° F are designated C195H(1,2,3) and C1100H(1,2,3) indicating 95- and 100-day exposure, respectively. The numbers in parentheses indicate replicate test specimens and therefore are not expected to have any significant differences when analyzed by HPSEC. The HPSEC designations for specimens C195H(1,2,3) and C1100H(1,2,3) are

- C95/180/95 = Batch 1, 95 days at 180° F/95% RH
- C100/180/95 = Batch 1, 100 days at 180° F/95% RH.

Batch 2 samples subjected to 200° F/95% RH + 7-day immersion in JP5 fuel at room temperature and tested at 180° F are designated A29FH(1,2,3) and A210FH(1,2,3) indicating 9- and 10-day exposure, respectively. The numbers in parentheses indicate replicate test specimens and therefore are not expected to have any significant differences when analyzed by HPSEC. The HPSEC designations for specimens A29FH(1,2,3) and A210FG(1,2,3) are

- A9/200/95 = Batch 2, 9 days at 200° F/95% RH + 7 days in JP5 fuel at RT
- A10/200/95 = Batch 2, 10 days at 200° F/95% RH + 7 days in JP5 fuel at RT.

Batch 2 samples subjected to 200° F/80% RH and tested at room temperature and designated D276R(1,2,3) and D280R(1,2,3) indicating 76- and 80-day exposure, respectively. The numbers

in parentheses indicate replicate test specimens and therefore are not expected to have any significant differences when analyzed by HPSEC. The HPSEC designations for specimens D276R(1,2,3) and D280R(1,2,3) are

- D76/200/80 = Batch 2, 76 days at 200° F/80% RH
- D80/200/80 = Batch 2, 80 days at 200° F/80% RH.

1.3 Requirements for HPSEC Analysis. HPSEC is used to determine polymer molecular weights (MW) and molecular weight distributions (MWD) and therefore may be used to study rubber reversion and estimate the extent of polymer degradation due to chain scission processes (i.e., by hydrolytic, thermal, mechanical and other environmental exposure or treatment). HPSEC separates molecules based upon their relative "size" in solution.[2] HPSEC chromatographic packing materials are microporous and chemically inert and are selected on the basis of their ability to separate or chromatographically resolve molecules in different size ranges. For linear polymer chains, the size of the polymer in solution generally increases with MW. Thus, larger molecules are "excluded" from more pores in the HPSEC packing material than smaller molecules and elute from HPSEC columns before smaller ones. Since the average polymer chain size or MW decreases during rubber reversion, one expects to observe an increase in the HPSEC elution or retention time of environmentally aged (degraded) polymer samples compared to unaged samples of the same material.

In order to perform HPSEC and obtain acceptable analytical results, a number of sampling and test condition criteria must be met. The polymer must be fully soluble in a solvent, which is compatible with the HPSEC columns and test equipment. The polymer solution must not be absorbed onto the column packing or contain any "gel" or suspended matter that might clog the column filters or packing material. The polymer must be stable (i.e., not degrade) in solution and during chromatographic analysis and detectable with linear (Beer's Law) response using either a refractive index (RI) or ultraviolet-visible (UV-vis) wavelength monitor. Tetrahydrofuran (THF)

---

[2] American Society for Testing and Materials. "Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography." *Annual Book of ASTM Standards*, ASTM D5296-92, vol. 08.03, ASTM: West Conshohocken, PA, 1998.

is commonly used for HPSEC analysis because it has a low viscosity and is a good solvent for many polymers, is compatible with HPSEC components, is transparent in the UV-visible spectrum, and is relatively safe to handle.

2. Solubility and Component Separation Study

The ester-based polyurethane rubber specimens are insoluble or poorly soluble in most organic solvents used for HPSEC analysis. The rubber could not be dissolved directly into THF, N,N-dimethylformamide (DMF), chloroform, toluene, or N-methylpyrolidone. However, the unaged rubber is fully soluble in a 50:50 (vol:vol) mixture of DMF and toluene. When DMF/toluene solutions of the rubber are added to THF, the solvents are miscible and the polymer remains soluble. Hence, samples for HPSEC analysis are prepared by first extracting rubber specimens with a 50:50 DMF/toluene mixture to dissolve the polymer and then diluting the resulting solutions with THF. The detailed procedure for sample preparation and isolation of the rubber from other specimen components is described in following text.

A section (approximately 0.25 g) not contaminated by ink markings is cut from near the center of the rubber test specimen and placed in a clean, ground-glass-stoppered, 25-ml Erlenmeyer flask. About 20 ml of a 50:50 DMF/toluene mixed solvent is added to the flask, and the specimen is allowed to soak in the solvent for at least one week with occasional vigorous mixing/shaking. (To reduce the possibility of polymer chain degradation during dissolution, the sample solutions are not heated.) The rubber in the Control specimens forms a black homogeneous solution. Insoluble components from the Control specimens include a layer of white fabric (reinforcement material); a thin layer of flexible, transparent film (interlayer?); a very thin, black, rubbery layer (coating?); and a black powdery residue (probably carbon black). The white fabric and transparent film retain their shapes after the solvent is removed. The black, rubbery layer, however, compresses into a small ball as the solvent evaporates.

The rubber solution is decanted from the Erlenmeyer flask into a glass centrifuge tube, and the flask and insoluble components are rinsed with small aliquot of THF (about 10 ml total).

After adding the THF rinse, the centrifuge tube is spun at about 30,000 g's on an ultracentrifuge to precipitate suspended carbon black, other particulates, and gels. The clarified solution is decanted from the centrifuge tube into a 50-ml volumetric flask, and THF is added to bring the solution volume up to the 50-ml mark. Depending upon the test specimen, the color of the solutions varied from light pink to dark pink (Table 1). After thorough mixing, about 4 ml of the solution is withdrawn by glass syringe from the volumetric flask, and filtered (0.45 μm, Millipore Fluoropore) into a glass vial that is capped for subsequent HPSEC analysis.

Table 1. Rubber Specimen Solution Characteristics and Composition

Specimen Designation	Solution Before Centrifugation	Solution After Centrifugation	Solids	Gel Fraction (F_{gel})
Control No. 1	homogeneous, black	light pink	Case 1	0
B115/180/80	heterogeneous, tinted	light pink	Case 2	0.599
B120/180/80	heterogeneous, tinted	dark pink	Case 2	0.486
C95/180/95	homogeneous, black	light pink	Case 1	0
C100/180/95	homogeneous, black	light pink	Case 1	0
Control No. 2	homogeneous, black	dark pink	Case 1	0
A9/200/95	heterogeneous, tinted	light pink	Case 2	0.524
A10/200/95	heterogeneous, tinted	light pink	Case 2	0.468
D76/200/80	homogeneous, black	light pink	Case 1	0
D80/200/80	homogeneous, black	dark pink	Case 1	0

By subtracting the dry weights of the insoluble components from the initial weight of the rubber specimen, the actual concentration of soluble components and hence quantity of rubber material injected for chromatographic analysis can be calculated. (This is important information for normalizing the chromatographs and estimating gel content from HPSEC data.) Insoluble materials remaining after the rubber extraction from the test specimens are categorized (Table 1) as either

- *Case 1.* Four primary components - white fabric; transparent film; black, rubbery layer; and black, powdery residue.

or

- *Case 2.* Swollen rubbery "gel" consisting of insoluble rubber combined with all the components noted in Case 1.

The total content or weight fraction of rubber (F_{rubber}) present in Case 1 specimens (i.e., fully soluble rubber) is calculated directly from weight measurements:

$$F_{rubber} = (W_i - W_f)/W_i, \tag{1}$$

where W_i is the initial weight of the test specimen and W_f is the final weight of the insoluble (solid) components separated and dried after solvent extraction (Case 1 specimens). The average weight fraction of rubber (F_{rubber}) determined in Batch 1 and Batch 2 test specimens (Case 1) is 0.776 and 0.705, respectively.

The gel content or weight fraction of gel (F_{gel}) in the rubber portion of the test specimen is determined using the formula

$$F_{gel} = 1 - (W_i - W_{insol})/(W_i \times F_{rubber}), \tag{2}$$

where W_{insol} is the final weight of the insoluble (solid) components separated and dried after solvent extraction (Case 2 specimens) and F_{rubber} is either 0.776 or 0.705 depending on the test specimen's Batch number. The gel contents (F_{gel}) of test specimens are listed in Table 1.

3. Experimental Procedure

3.1 HPSEC Sample Preparation. For preliminary HPSEC studies, sample solutions were prepared according to the procedure described in the "Solubility and Component Separation Study" section. To facilitate rubber extraction and lower solution concentrations for the final HPSEC analysis, specimen sample sizes and final solution volumes were reduced from 0.25 to 0.05 g and from 50 ml to 30 ml, respectively, which offered maximum solution concentrations corresponding to approximately 1.2 g/l based upon the amount of rubber contained in the

6

specimens and assuming full solubility of the rubber. Otherwise, the sample preparation procedure was identical.

HPSEC column calibration for polymer MW analysis requires the use of narrow MWD polystyrene standards.[2] Solutions containing a "cocktail" of polystyrene standards are prepared with THF as the solvent in 50-ml volumetric flasks. The average MW values of the standards in each solution are separated by at least 1 decade:

- Standard Solution No. 1: 10,000; 97,200; and 1,000,000 g/mol.
- Standard Solution No. 2: 2,000; 19,800; 200,000; and 2,000,000 g/mol.

The concentration of each polystyrene standard in solution is about 0.3 g/L. The calibration standard solutions are filtered (0.45 μl, Millipore Fluoropore) using a syringe adapter into glass vials capped to prevent solvent evaporation.

3.2 HPSEC Operating Conditions and Calibration. A Waters (Waters Associates, Milford, MA) HPLC/SEC Chromatography and Data Acquisition System with Millennium software is used for HPSEC study. The system includes the following Waters components – Model 510 Pump, Model 717 Auto Sampler (injector), Model 486 Tunable Absorbance Detector (wavelength set at 254 nm), Model 410 Differential Refractometer and a set of five micro-Styragel columns (1,000,000 Å; 100,000 Å; 10,000 Å; 500 Å; and 100 Å). The mobile phase (THF) is degassed with helium to prevent peroxide formation and the column temperature is maintained at 40° C in a block oven. HPSEC operating conditions are summarized as follows:

- Mobile Phase: THF (tetrahydrofuran)
- Flow Rate: 1 ml/min
- Sample Injection Volume: 100 μl
- Detectors: RI (refractive index) and UV (254 nm) detector.

---

[2] American Society for Testing and Materials. "Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography." *Annual Book of ASTM Standards*, ASTM D5296-92, vol. 08.03, ASTM: West Conshohocken, PA, 1998.

HPSEC calibration using the polystyrene standards[2] shows that the system is operating properly and the columns have good resolution over the MW range of 2,000 to 2,000,000 g/mol (Daltons). The polystyrene standard chromatograms and resulting HPSEC calibration curve are shown in Figures 1 and 2, respectively.
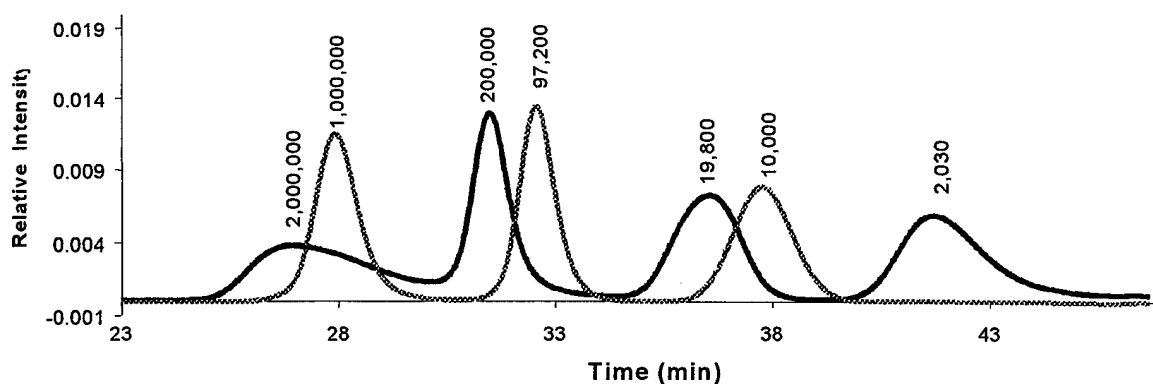

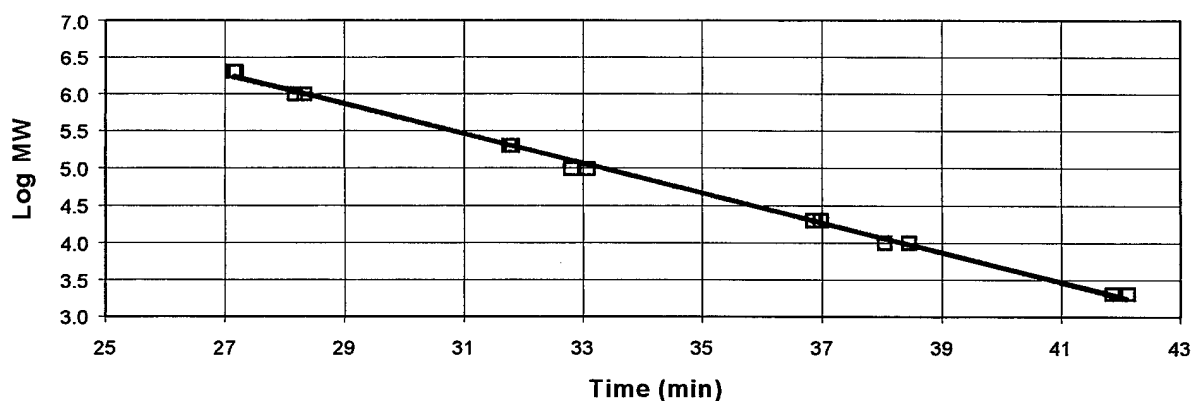Figure 1. HPSEC Chromatograms of Polystyrene Standards.

Figure 2. HPSEC Polystyrene Calibration Curve.

3.3 HPSEC Analysis. HPSEC sample preparation, operating conditions, calibration, and analysis procedures employed in the study are based on ASTM Standard Test Method D5296-92. The ester-based polyurethane rubber MW and MWD values are calculated from chromatograms

[2] American Society for Testing and Materials. "Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography." *Annual Book of ASTM Standards*, ASTM D5296-92, vol. 08.03, ASTM: West Conshohocken, PA, 1998.

obtained using the refractive index (RI) detector and the polystyrene standard calibration curve shown in Figure 2. Therefore, MW values obtained for the rubber specimens described in this report are not absolute values, but rather are relative to those of polystyrene molecules having the same size as the rubber molecules in THF solution. The reported MW values are "apparent" molecular weights but should provide a useful measure of relative differences and changes in average polymer chain length. Additional assumptions that depart from ASTM D5296 and may contribute to errors in MW analysis are that (1) rubber molecules are the primary sample components producing an RI response, (2) all rubber molecules have the same RI responsiveness (i.e., concentration dependence) regardless of MW, and (3) the "cut-off" for polymer data acquisition is 2,000 g/mol (i.e., the lowest MW calibration standard). Considering the assumptions, it is interesting to note that the "apparent" MW results reported (Table 2) for rubber materials in Control Nos. 1 and 2 specimens are similar to values generally expected for linear, high MW polyurethanes synthesized by step-growth polymerization. It is also noted that the HPSEC analyses obtained for two different test specimens (identified by the letters "a" and "b" in Table 2) subjected to the same aging conditions are generally in very good agreement. Hence, the results are encouraging in applying HPSEC to monitor relative changes in the MW's of rubber in test specimens subjected to accelerated environmental aging.

HPSEC chromatograms for the rubber Control specimens are compared in Figures 3 and 4. The rubber in specimens Control No. 1 and Control No. 2 are fully soluble in the test solution, and the amounts (mass = 0.078 mg) injected for HPSEC analysis are essentially the same. Differences between the control specimens are immediately obvious. The HPSEC peak (Figure 3) for Control No. 2 occurs at a slightly earlier retention time compared to that of Control No. 1, which suggests that the peak- and weight-average molecular weight values M_p and M_w, respectively, for Control No. 2 are somewhat higher than for Control No. 1. Chromatograms obtained using UV detection (Figure 4) show that both samples probably contain low MW additives (37–46 minutes) that absorb strongly in the UV and have equivalent polystyrene molecular weights in the 1,000- to 15,000-g/mol region with a major component at about 5,000 g/mol. Differences apparent in the heights of the polymer peaks (32–34 minutes) relative

Table 2. Rubber Specimen Aging and HPSEC Analysis

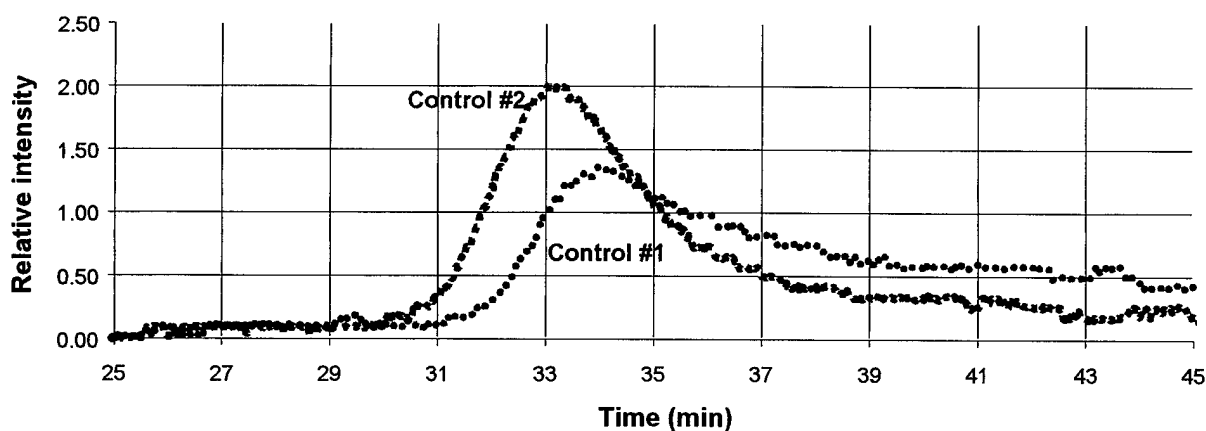| Specimen		Aging Conditions			HPSEC Analysis				
Sample Identification	Batch No.	Time (days)	Temperature (°F)	Humidity (% RH)	M_p	M_w	M_n	M_w/M_n	Gel (F_{gel})
Control No. 1a	1	0	na	na	76,000	69,200	43,500	1.59	−0.053
Control No. 1b	1	0	na	na	97,000	83,500	58,100	1.44	0.053
B115/180/80a	1	115	180	80	24,000	36,900	15,600	2.37	0.621
B115/180/80b	1	115	180	80	27,000	31,000	14,100	2.20	0.628
B120/180/81a	1	120	180	80	30,000	32,700	14,400	2.27	0.447
B120/180/81b	1	120	180	80	31,000	30,000	11,300	2.65	0.464
C95/180/95a	1	95	180	95	16,000	14,500	7,900	1.84	0.239
C95/180/95b	1	95	180	95	12,000	15,200	7,600	2.00	0.125
C100/180/95a	1	100	180	95	11,000	13,600	7,400	1.84	0.151
C100/180/95b	1	100	180	95	8,000	10,800	6,300	1.71	0.222
Control No. 2a	2	0	na	na	103,000	92,300	39,400	2.34	0.019
Control No. 2b	2	0	na	na	106,000	92,500	23,300	3.93	−0.019
A9/200/95a	2	9	200	95	66,000	52,000	19,200	2.71	0.495
A9/200/95b	2	9	200	95	61,000	54,900	19,800	2.77	0.482
A10/200/95a	2	10	200	95	68,000	55,700	23,100	2.41	0.431
A10/200/95b	2	10	200	95	55,000	53,800	24,700	2.18	0.529
D76/200/80a	2	76	200	80	4,000	5,600	4,100	1.42	−0.054
D76/200/80b	2	76	200	80	3,900	5,300	3,900	1.36	0.144
D80/200/80a	2	80	200	80	4,000	5,800	4,000	1.45	0.109
D76/200/80b	2	80	200	80	3,900	5,900	4,100	1.44	0.075

Figure 3. HPSEC Chromatograms of Control No. 1 and Control No. 2 Rubber Samples (RI Detector).
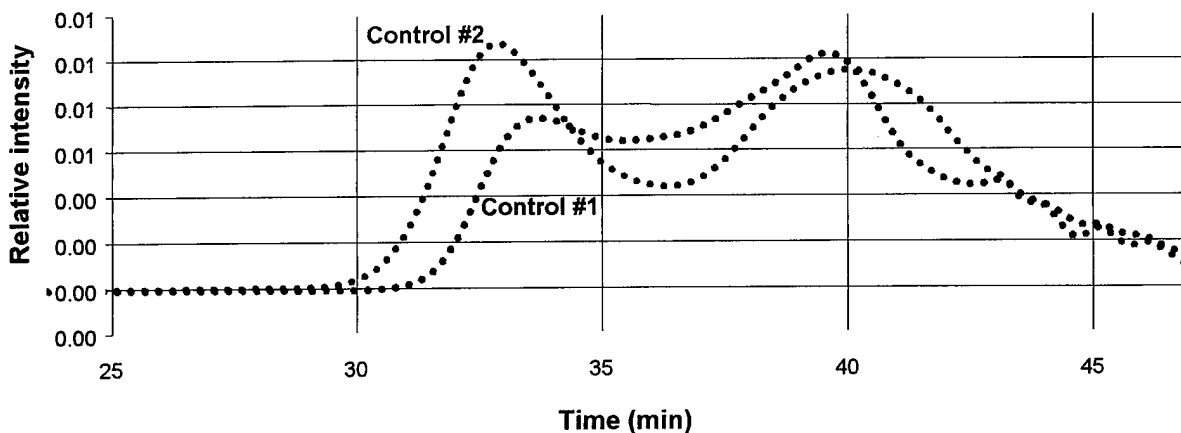
Figure 4. HPSEC Chromatograms of Control No. 1 and Control No. 2 Rubber Samples (UV Detector).

to the highest peaks of the low MW additives (assuming the chemical compositions of the additives in the controls are similar) also indicate that relative amounts of low MW additives in the control samples are different. The observation that peaks do not occur for such low MW additives with RI detection not only indicates that the additives absorb strongly in the UV but also suggests that the concentration of such additives relative to the principal polymer component (rubber) is not very high (i.e., probably less than 10% by weight). Indeed the "tailing" of the high MW rubber peaks for the control samples noted in Figure 3 might be attributable to low MW additives that are present as minor constituents in the rubber formulations.

Due to the interference of the low MW additives in chromatograms obtained with UV detection, only data obtained with RI detection can be used for calculating "apparent" MW values. Differential and cumulative MWD curves interpreted from RI HPSEC chromatograms of Control Nos. 1 and 2 are shown in Figures 5 and 6, respectively. The abscissa scale is represented in logarithm (base 10) MW (grams per mole or Dalton) units. The differential MWD plot (left ordinate) shows that the peak MW value (M_p) of Control No. 2 (ca. 103,000 g/mol) is appreciably higher than that of Control No. 1 (75,800 g/mol). Similarly, the weight-average MW (M_w) of Control No. 2 is higher than that of Control No. 1. The control samples also differ in
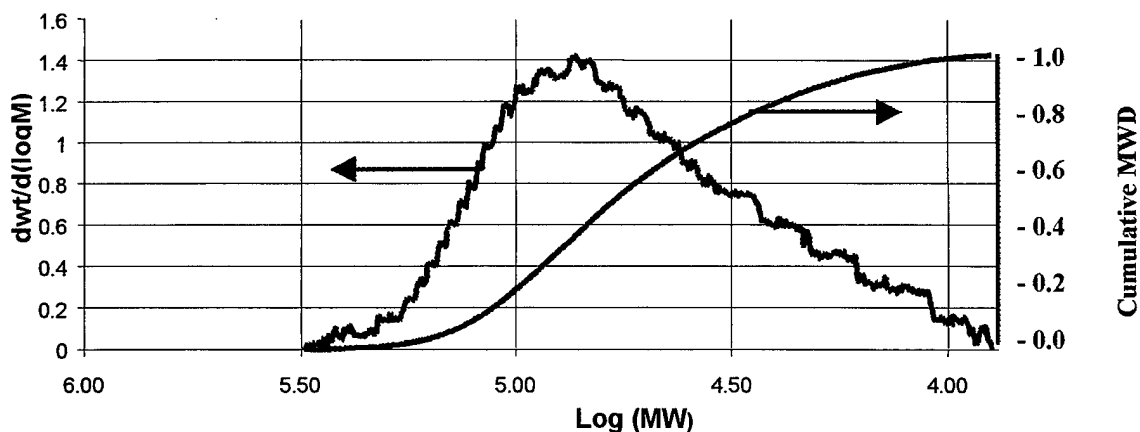
11

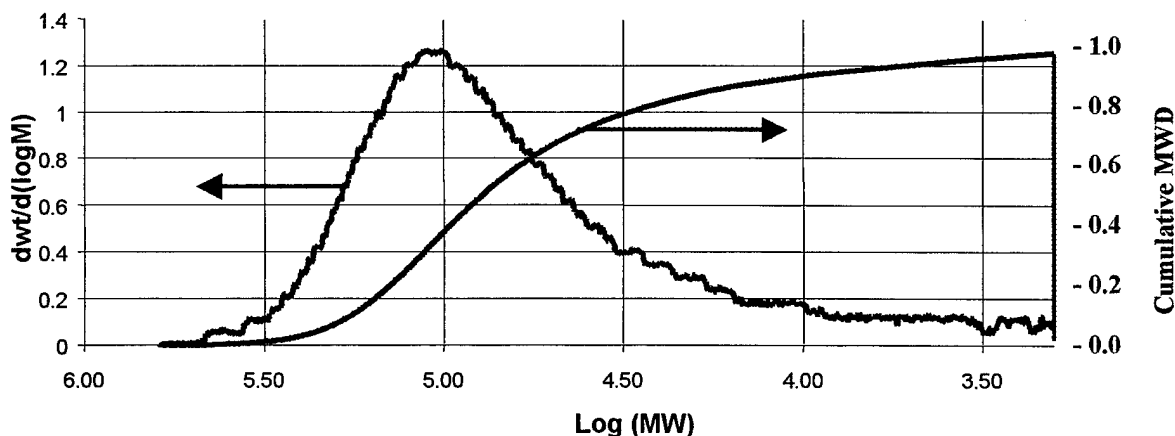**Figure 5. Differential and Cumulative MWD Curves for Control No. 1.**

Figure 6. Differential and Cumulative MWD Curves for Control No. 2.

that the MWD of Control No. 2 is somewhat broader than that of Control No. 1 as indicated by Control No. 2's lower number-average MW (M_n) and higher M_w/M_n ratio values.

The cumulative distribution curve (right ordinate) is a plot of log (MW) vs. weight fraction (0–1 scale) of material analyzed. Accordingly, about 50% by weight of soluble material in Control No. 1 has an "apparent" MW greater than 64,900 g/mol. By comparison, Control No. 2 has 50% of its material with an MW greater than 87,100 g/mol. The amount of material having an MW less than 20,000 g/mol in Control Nos. 1 and 2 is 8.2% and 10.1%, respectively. This

12

result is consistent with the earlier observation that the concentration of the UV-absorbing, low-MW additives in the rubber specimens is relatively low.

Comparisons of HPSEC chromatograms obtained from the analysis of the unaged Control and accelerated environmentally aged test specimens show dramatic differences (Figures 7–10). Accelerated aging significantly affects the peak areas (i.e., amount of soluble materials) and the peak positions and shapes (i.e., MW and MWD). Reductions in peak areas observed for test specimens aged under higher relative humidity (95% RH) conditions (C100/180/95 vs. Control No. 1 in Figures 7–8 and A10/200/95 vs. Control No. 2 in Figures 9–10) are directly proportional to reductions in the mass or amount of soluble materials injected onto the column and consistent with the formation of insoluble rubber materials (gel) noted earlier. The shifts of peak maxima to longer retention times (lower MW) with increasing aging times are indicative of significant polymer chain degradation or rubber reversion effects. At long aging times and 80% RH, the initial high MW polymer peaks totally disappear and over 90% by weight of the remaining materials have MW's less than 20,000 g/mol (C115/180/80 in Figures 7–8 and D76/200/80 in Figures 9–10). Differential MWD plots (Figures 11–12) clearly illustrate the effect of accelerated aging on the rubber sample molecular weight. "Apparent" MW values are summarized in Table 2.
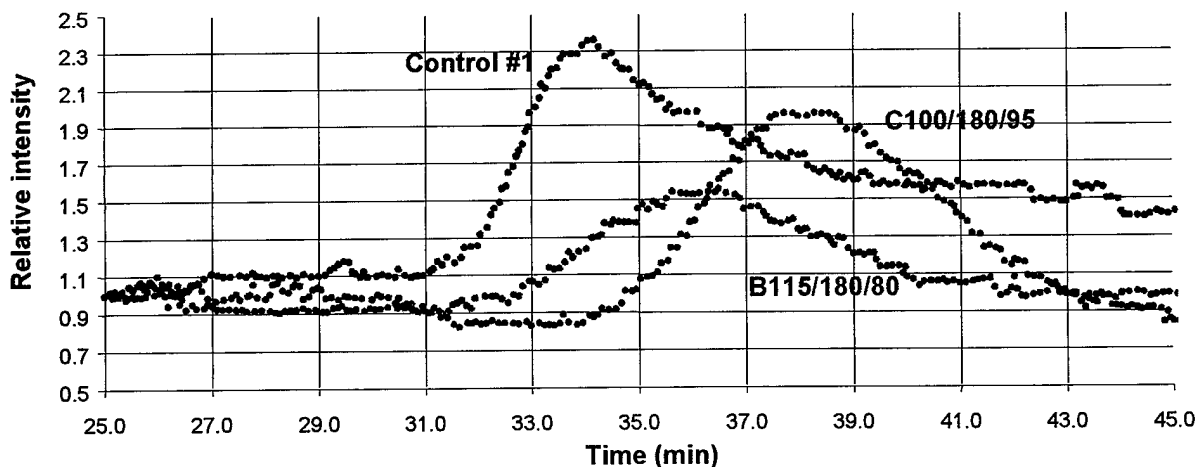

Figure 7. HPSEC Chromatograms of Control No. 1, B115/180/80 and C100/180/95 (RI Detector).
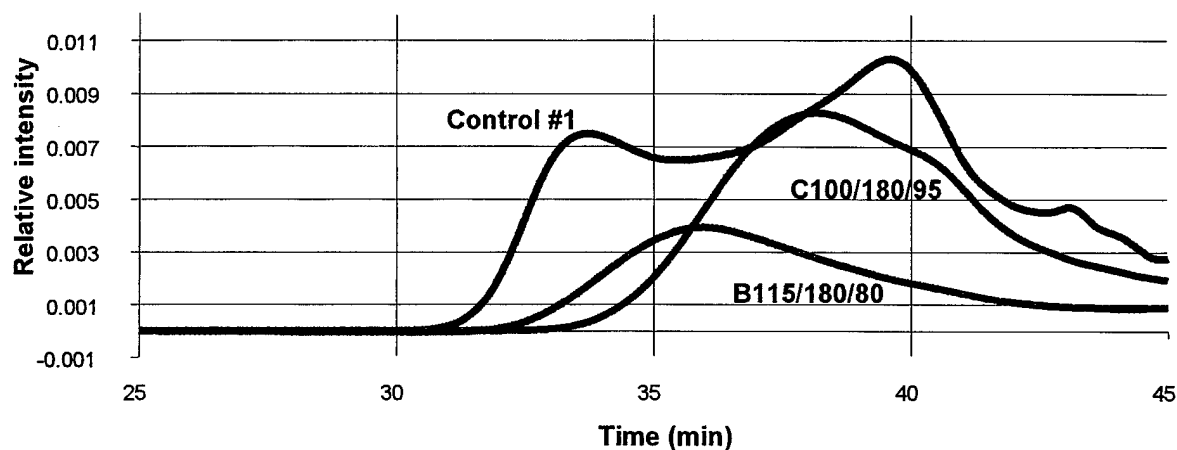
Figure 8. HPSEC Chromatograms of Control No. 1, B115/180/80 and C100/180/95
(UV Detector).

Figure 9. HPSEC Chromatograms of Control No. 2, A10/200/95 and D76/200/80
(RI Detector).

Assuming that the integrated peak area is directly proportional to the mass of sample injected and that the weight fraction of insoluble (Case 1) components $(1 - F_{rubber})$ is constant for all specimens from the same batch and independent of the excised sample's location or size, the insoluble polymer or weight fraction of gel (F_{gel}) in the rubber portion of test specimens may be estimated from HPSEC data:
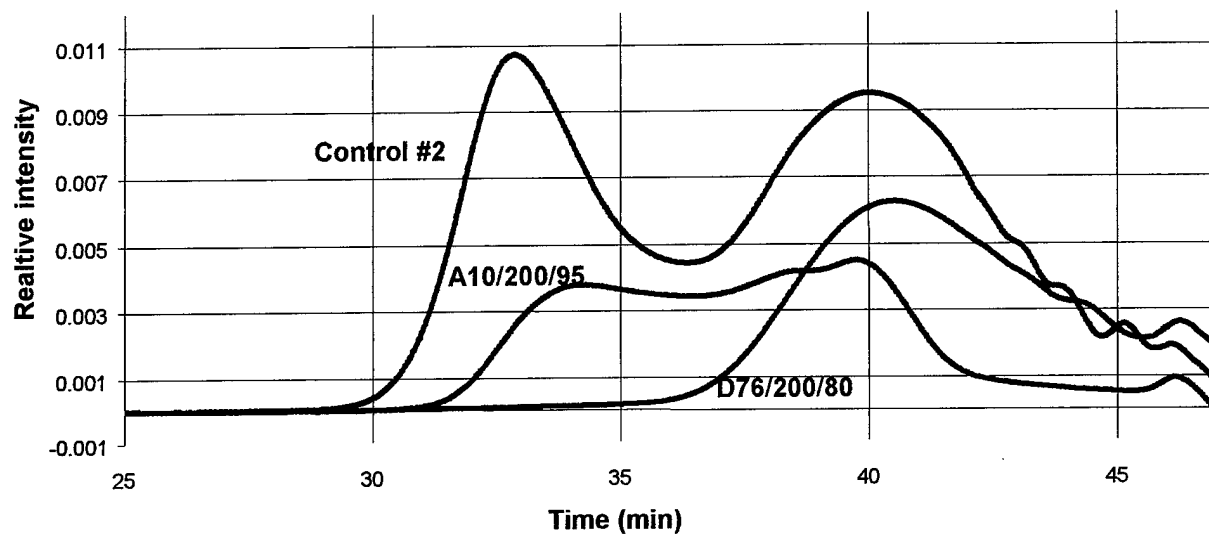
14

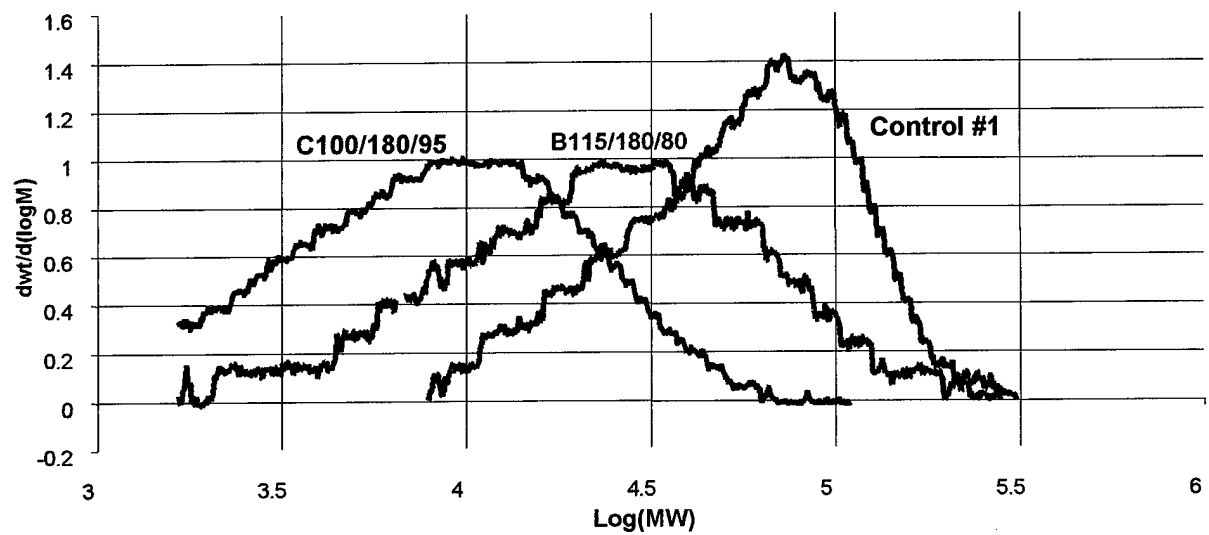**Figure 10. HPSEC Chromatograms of Control No. 2, A10/200/95 and D76/200/80 (UV Detector).**

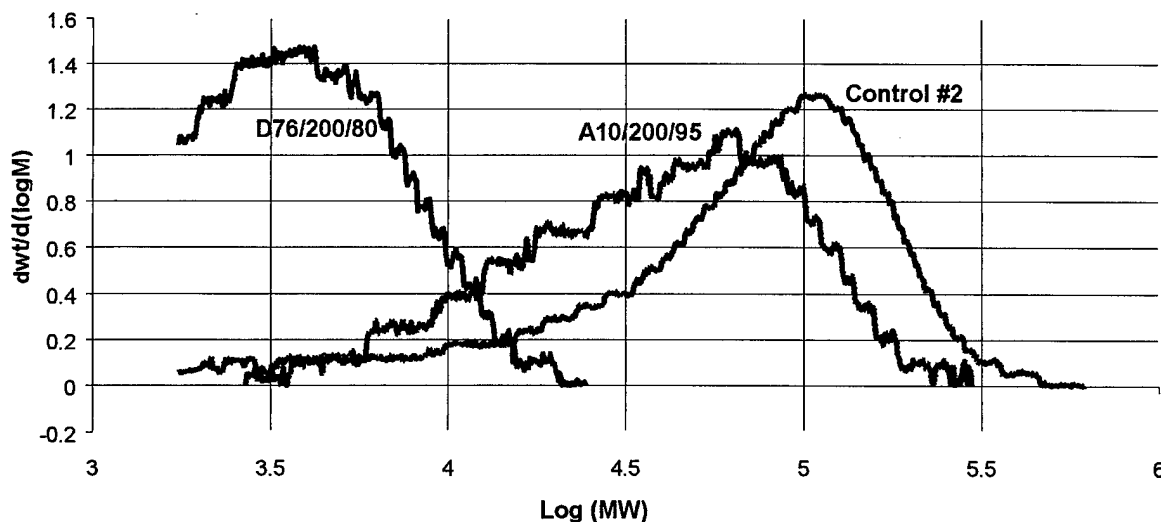**Figure 11. Differential MWD Curves for Control No. 1, B115/180/80 and C100/180/95.**

15

Figure 12. Differential MWD Curves for Control No. 2, A10/200/95 and D76/200/80.

$$F_{gel} = 1 - W_c \times A_s/(W_s \times A_c), \tag{3}$$

where W_c and A_c are the initial weight and integrated peak area of the control specimen and W_s and A_s are the initial weight and integrated peak area of the aged test specimen from the same batch.
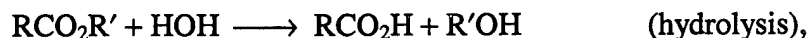
Gel content (F_{gel}) values estimated from HPSEC data are included in Table 2. The agreement between different test specimens (designated by the letters "a" and "b") subjected to the same aging conditions is remarkably good considering the small sample sizes and assumption of specimen uniformity. The average variation in F_{gel} for specimens subjected to the same aging condition is 0.07. F_{gel} values indicated for the control specimens reflect the statistical error in measurements. The control specimens do not contain measurable gel. Gel fractions calculated from HPSEC data are in good agreement with F_{gel} values determined gravimetrically (Table 1) for specimens actually found to contain gel. Specimens subjected to more severe degradation conditions and showing large concentrations of low MW products (i.e., $M_n < 10,000$) appear to contain small amounts of gel. The same specimens however did not show any gel when analyzed gravimetrically. It is possible that F_{gel} values calculated from equation 3 actually may be more correct than those determined gravimetrically. The gravimetric analysis procedure may

16

neglect to account for "soluble" microgel and therefore indicate no gel when small amounts of soluble (perhaps degraded insoluble gel) microgel are present. Such microgel would probably be removed during HPLC sample preparation and therefore corrected for in the HPSEC procedure.
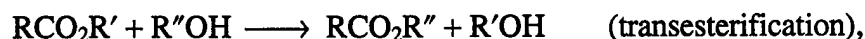
4. Conclusions and Comments

HPSEC and the procedures described in this report for sample preparation and gel determination are very useful in analyzing the effects of accelerated environmental aging on the polymer chain structure of ester-based polyurethane test specimens. The repeatability of the HPSEC sample preparation procedure and analyses are excellent. Compositional and MW differences in control rubber specimens from different batches are clearly evident. Accelerated aging of test specimens induces gel (insoluble polymer) formation and polymer chain degradation. To be definitive about the cause(s) and progression of such changes, the exact chemical compositions of the specimen rubber formulations and a larger number of test specimens over the entire range of aging conditions would need to be analyzed. Nevertheless, based on the limited number of specimens analyzed, a number of conclusions are possible:

(1) *Polymer chain degradation occurs when the rubber test specimens are exposed to moisture at elevated temperatures, and it increases with exposure time.* Such behavior is endemic for ester-based polymer materials and is usually accelerated in the presence of strong acids and inorganic salts. Even in the absence of a strong acid, ester linkages may undergo hydrolysis slowly to form carboxylic acid- and alcohol-terminated groups or undergo a transesterification reaction in which one ester group linkage is exchanged for another or reacted with an alcohol such as indicated below:
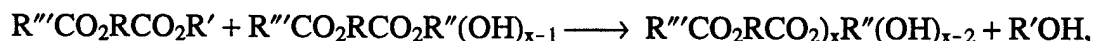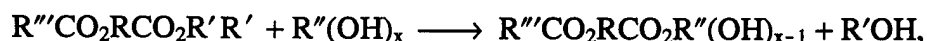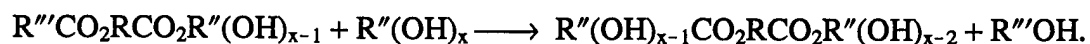
$$RCO_2R' + HOH \longrightarrow RCO_2H + R'OH \qquad \text{(hydrolysis),}$$

and

$$RCO_2R' + R''OH \longrightarrow RCO_2R'' + R'OH \qquad \text{(transesterification),}$$

where R and R′ represent portions of the polymer chain jointed through the ester ($-CO_2-$) linkage, and R″ may be a section of hydrolyzed polymer chain or another hydroxyl-containing ($-OH$) molecule. The reaction with water (hydrolysis) inevitably results in polymer chain scission and a decrease in MW. Assuming the distribution of ester linkages is statistically uniform, high MW polymer chains will have more ester groups and therefore are more likely to undergo chain scission than lower MW polymers. Polymer chains with MW's of 100,000 g/mol may have as many as 1,000 ester linkages. Hence, the hydrolysis of only one segment per polymer chain backbone would decrease the average MW from 100,00 to 50,000 g/mol for a statistical distribution of polymer chains. The use of HPSEC allows one to readily distinguish such MW changes, even if the effect is only 1 part per thousand. Transesterification also may lead to a net decrease in MW if the size or molecular weight of R″ is appreciably less than that of R′.

(2) *Both polymer crosslinking (gelation) and polymer chain degradation reactions occur during the early stages of accelerated environmental aging.* The presence of multifunctional reactive groups (e.g., trifunctional hydroxyl-, amino-, or isocyanate terminated groups) during polyester polyurethane polymerization generally produces highly branched or crosslinked polymers which swell in solution and are insoluble. The presence of such multifunctional components added and unreacted during rubber formation may provide avenues to crosslinking and hence gel formation during accelerated aging; e.g., through multiple transesterification reactions:

$$R'''CO_2RCO_2R'R' + R''(OH)_x \longrightarrow R'''CO_2RCO_2R''(OH)_{x-1} + R'OH,$$

$$R'''CO_2RCO_2R' + R'''CO_2RCO_2R''(OH)_{x-1} \longrightarrow R'''CO_2RCO_2)_xR''(OH)_{x-2} + R'OH,$$

and

$$R'''CO_2RCO_2R''(OH)_{x-1} + R''(OH)_x \longrightarrow R''(OH)_{x-1}CO_2RCO_2R''(OH)_{x-2} + R'''OH.$$

18

Continuing transesterification with excess $R''(OH)_x$ could lead to the formation of crosslinked, insoluble "gel" and soluble low MW residual products (e.g., $R'OH$ and $R'''OH$) particularly if the multifunctional additive $R''(OH)_x$ is designed to be highly reactive in the presence of moisture and at elevated temperatures.

(3) *As the time and severity of aging conditions (temperature and humidity) increase, gel formed during the early stages of exposure apparently decreases and the MW of the soluble materials continues to decrease.*

- The change in MW and gel content for specimens exposed to JP5 jet fuel and aged for 10 days at 200° F and 95% RH and for 120 days at 180° F and 80% RH is about the same (i.e., M_w decreases about 40,000 g/mol).

- Exposure of test specimens to higher moisture levels (% RH) during environmental aging has a very significant effect on polymer degradation (comparison of B115/180/80 and B120/180/80 with C95/180/95 and C100/180/95 HPSEC test data).

- A temperature increase from 180° F to 200° F has a significant impact on the degradation of polymers in rubber specimens (comparison of MW data obtained for specimens aged 80 days at 200° F and 80% RH and for 95 days at 180° F and 95% RH).

(4) *Given the data available, it is not possible to tell whether Batch 1 or Batch 2 specimens have better environmental stability.* Accelerated environmental aging certainly has a major impact on the MW of the rubber and on gel formation. Crosslinking associated with gel formation may actually improve certain physical properties, such as tensile strength and hardness, while compromising other properties, such as flexural strength and crack and tear resistance. Decreasing MW almost always results in reduced mechanical properties and poorer rubber elasticity. Specimens C95/180/95, C100/180/95, D76/200/80, and D80/200/80 will undoubtedly have unacceptable physical and mechanical properties for fuel bladder and containment applications.

INTENTIONALLY LEFT BLANK.

NO. OF COPIES	ORGANIZATION	NO. OF COPIES	ORGANIZATION
2	DEFENSE TECHNICAL INFORMATION CENTER DTIC DDA 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218	1	DIRECTOR US ARMY RESEARCH LAB AMSRL D D R SMITH 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	HQDA DAMO FDQ D SCHMIDT 400 ARMY PENTAGON WASHINGTON DC 20310-0460	1	DIRECTOR US ARMY RESEARCH LAB AMSRL DD 2800 POWDER MILL RD ADELPHI MD 20783-1197
1	OSD OUSD(A&T)/ODDDR&E(R) R J TREW THE PENTAGON WASHINGTON DC 20301-7100	1	DIRECTOR US ARMY RESEARCH LAB AMSRL CS AS (RECORDS MGMT) 2800 POWDER MILL RD ADELPHI MD 20783-1145
1	DPTY CG FOR RDA US ARMY MATERIEL CMD AMCRDA 5001 EISENHOWER AVE ALEXANDRIA VA 22333-0001	3	DIRECTOR US ARMY RESEARCH LAB AMSRL CI LL 2800 POWDER MILL RD ADELPHI MD 20783-1145
1	INST FOR ADVNCD TCHNLGY THE UNIV OF TEXAS AT AUSTIN PO BOX 202797 AUSTIN TX 78720-2797		ABERDEEN PROVING GROUND
1	DARPA B KASPAR 3701 N FAIRFAX DR ARLINGTON VA 22203-1714	4	DIR USARL AMSRL CI LP (BLDG 305)
1	NAVAL SURFACE WARFARE CTR CODE B07 J PENNELLA 17320 DAHLGREN RD BLDG 1470 RM 1101 DAHLGREN VA 22448-5100		
1	US MILITARY ACADEMY MATH SCI CTR OF EXCELLENCE DEPT OF MATHEMATICAL SCI MADN MATH THAYER HALL WEST POINT NY 10996-1786		

NO. OF
COPIES   ORGANIZATION

           <u>ABERDEEN PROVING GROUND</u>

   50   DIR USARL
           AMSRL WM MA
           E NAPADENSKY

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project(0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 2000	Final, Nov 97 - Jul 98

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
HPSEC Analysis of Ester-Based Polyurethane Rubber Materials	77GHW1

6. AUTHOR(S)

Eugene Napadensky, Gary L. Hagnauer, Amy Kinkennon, and Donald T. Rorabaugh*

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
U.S. Army Research Laboratory ATTN: AMSRL-WM-MA Aberdeen Proving Ground, MD 21005-5069	ARL-TR-2201

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)	10.SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

*U.S. Army Armament Research, Development, and Engineering Center.

12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
Approved for public release; distribution is unlimited.	

13. ABSTRACT (Maximum 200 words)

The work described in this report contributes to a larger study conducted by the U.S. Army Tank-automotive and Armaments Command (TACOM) at Picatinny Arsenal, NJ, to evaluate the environmental and operational stability of candidate commercial polyester-polyurethane rubber materials for possible fuel bladder and containment applications. High-performance size-exclusion chromatography (HPSEC) techniques are employed to analyze and help understand the effects of accelerated environmental exposure on the average molecular weights (MW) and molecular weight distributions (MWD) of the rubber in selected test specimens. A special test method and sample preparation procedures to extract and isolate the soluble polymer in test specimens from coating, interlayer, fabric, and carbon reinforcement components are described. HPSEC separates polymer molecules according to their relative "sizes" in solution and therefore is very useful in studying rubber reversion and estimating the extent of polymer degradation due to chain scission processes. Exposure to elevated temperature and moisture content (percent relative humidity) accelerate sample degradation. As the aging time and severity of aging conditions increase, gel formed during the early stages of exposure disappears and the MW of soluble materials continues to decrease. The chemical mechanism for polymer chain degradation and possible cause and consequences of the gelation effect are discussed.

14. SUBJECT TERMS		15. NUMBER OF PAGES
HPSEC, GPC, polyurethane rubber, polyurethane, chain degradation analysis		27
		16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18   298-102

INTENTIONALLY LEFT BLANK.

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. ARL Report Number/Author_____ARL-TR-2201 (Napadensky)_____ Date of Report _April 2000_

2. Date Report Received _____

3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) _____

_____

_____

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) _____

_____

_____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. _____

_____

_____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) _____

_____

_____

_____

Organization

CURRENT   Name   E-mail Name
ADDRESS
               Street or P.O. Box No.

               City, State, Zip Code

7. If indicating a Change of Address or Address Correction, please provide the Current or Correct address above and the Old or Incorrect address below.

Organization

OLD   Name
ADDRESS
               Street or P.O. Box No.

               City, State, Zip Code

(Remove this sheet, fold as indicated, tape closed, and mail.)
(DO NOT STAPLE)